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THE CERTIFICATION OF THORIUM AND URANIUM CONCENTRATIONS IN CCRMP REFERENCE MATERIAL OKA-2

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THE CERTIFICATION OF THORIUM AND URANIUM CONCENTRATIONS IN CCRMP REFERENCE MATERIAL OKA-2

C.W. Smith*, H.F. Steger** and W.S. Bowman***

ABSTRACT

OKA-2 is a compositional reference material prepared from samples from a britholite deposit near Oka, Quebec. The samples were collected by the Radiation Geophysics Section, GSC in aid of an IAEA project to produce a gamma-ray spectrometry calibration material for thorium measurements. The material was subsequently donated to CCRMP as a candidate reference material for thorium and rare-earth elements, and as source material to prepare the IAEA reference material by silica dilution.

The results of separate measurement programs by CCRMP and IAEA for thorium, uranium and potassium in OKA-2 are presented herein. Since the consensus values from the two programs were in agreement, the results were combined by CCRMP to obtain recommended concentration values.

The recommended values for thorium, uranium, and potassium are 2.893±0.058 % Th, 218.6±8.2 µg/g U and 0.344±0.022 % K. The uncertainties are 95% confidence interval estimates for the consensus values of 29, 27 and 8 accepted laboratory sets, respectively. The values for thorium and uranium are certifiable by CCRMP criteria.

The concurrence of radiometric and chemical/physical measurements of thorium and uranium indicates that radiometric equilibrium exists in the ^{232}Th and ^{238}U decay series. The thorium/uranium ratio met the IAEA requirements for source material for the preparation of a gamma-ray calibration reference material. This preparation was subsequently carried out at the CCRMP facilities, Mineral Sciences Laboratories in November, 1986.

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CERTIFICATION DES CONCENTRATIONS DE THORIUM ET D'URANIUM DANS LE MATÉRIEL DE RÉFÉRENCE OKA-2 DU PCMRC

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RÉSUMÉ

OKA-2 est un matériau de référence de composition préparé à partir d'échantillons provenant d'un dépôt de britholite localisé près d'Oka, Québec. Les échantillons ont été ramassés par la Section de géophysique de radiation GSC, avec l'aide d'un projet AIEA, de façon à produire un matériel de calibration par spectrométrie au rayon-gamma pour des mesures de thorium. Le matériel a été par la suite donné au PCMRC à titre de matériau de référence candidat pour le thorium et les éléments de terre-rare et à titre de matériel source pour préparer le matériel de référence AIEA par dilution à la silice.

Les résultats des programmes séparés de mesures du PCMRC et de l'AIEA pour le thorium, l'uranium et le potassium présents dans l'Oka-2 sont présentés. Puisque les valeurs consensus tirées des deux programmes étaient concordantes, les résultats ont été combinés par le PCMRC pour obtenir les valeurs de concentration recommandées.

Les valeurs recommandées pour le thorium, l'uranium et le potassium sont 2,893±0,058 % Th, 218,6±8,2 µg/g U et 0,344±0,022 % K. Les limites d'incertitude pour les valeurs consensus de 29, 27 et 8 de chacun des ensembles acceptés de laboratoire sont à des estimations d'intervales de confiance de 95 %. Les valeurs pour le thorium et l'uranium sont certifiables selon les critères du PCMRC.

La concordance des mesures radiométriques et physico-chimiques du thorium et de l'uranium indique qu'un équilibre radiométrique existe dans la série de désintégration du ^{232}Th et du ^{238}U. Le rapport

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thorium/uranium rencontre les exigences de l'AIEA pour le matériel source pour la préparation d'un matériel de calibration de référence au rayon-gamma. Cette préparation a été subséquemment réalisée aux installations PCMRC, Laboratoires des sciences minérales, en novembre, 1986.

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INTRODUCTION

OKA-2 is a comminuted and homogenized sample of britholite mineral (with some gangue inclusions) from a known occurrence near Oka, Quebec. The britholite mineral from Oka has been described as thorium-bearing cerian silicate apatite with a probable formulation: (Ca, Ce etc., Th, Mg, Fe, Na, Ti)$_5$[(P, Si, Al)O$_{4,3}$(OH, F)] (1). The sample was collected from massive material from the Dufresne Hill property which has been described elsewhere (2).

The britholite sample was collected by a field party from the Resource Geophysics and Geochemistry Division, Geological Survey of Canada, in assistance of an International Atomic Energy Agency (IAEA) project to obtain material that would be suitable for a gamma-ray spectrometer calibration standard for thorium measurements. A principle requirement for this material was that the thorium to uranium and thorium to potassium ratios be sufficiently high that the gamma-ray emissions from uranium-daughter isotopes and potassium-40 would have a negligible contribution to the total emissions. A quantitative minimum acceptable concentration ratio for equivalent thorium to equivalent uranium was defined as 100 (3). A series of gamma-ray measurements of the rock complex demonstrated that the Oka material had an acceptable thorium to uranium ratio (3).

The Canadian Certified Reference Materials Project (CCRMP) of CANMET was interested in OKA-2 both from the viewpoint of supporting the IAEA project for thorium, and as a potentially useful Canadian compositional reference material, particularly for the lanthanide series elements. The Geological Survey subsequently donated the britholite sample to CCRMP with the understanding that a suitable quantity of the prepared material would be made available to prepare the more dilute IAEA thorium calibration material to be known as RGTh-1.

OKA-2 was prepared in February 1985, and samples were subsequently distributed to participating laboratories in the measurement programs of the IAEA and CCRMP. Results for thorium, uranium and potassium from both programs were combined to determine the recommended concentration values and their uncertainties.

PREPARATION OF OKA-2

The rock sample of 79.4 kg was comminuted in a ball mill in three stages and then sieved through a Tyler 200 mesh screen to yield 75.5 kg of a sub 75-μm product. The undersize material was blended in a 540-L capacity conical blender for 16 h and then bottled in 102(±2)-g units.

A wet screen analysis of OKA-2 is given in Table 1. The approximate chemical composition of OKA-2, which has been estimated from contributions from several laboratories is reported in Table 2.

Prior to the interlaboratory measurement programs, the bottled stock was sampled to test the homogeneity of the material. The stock of 780 bottles was segmented into 15 equal-sized units in the order of bottling, and one bottle from each unit was sampled. Three subsamples from each bottle were then taken for thorium measurements by X-ray fluorescence spectrometry. The samples were measured as loose-packed powders in Mylar® -windowed X-ray sample cups, and results are presented in Table 3.

The distribution of the X-ray measurements of thorium were analysed by one-way classification analysis of variance (4). The results, presented in Table 4, show no evidence for inhomogeneity; consequently, OKA-2 was regarded as a candidate reference material for thorium.

INTERLABORATORY MEASUREMENT PROGRAMS

Both CCRMP and IAEA coordinated measurement programs for the certification of OKA-2. The CCRMP program incorporated the measurement of lanthanide elements, thorium and uranium[1], and the IAEA program requested analyses of thorium, uranium, uranium/radium ratio and potassium in accord with the objective of the use of OKA-2 to prepare the thorium gamma-ray calibration material, RGTH-1[2].

Participating laboratories were each provided with one randomly selected bottle of the stock of OKA-2 and were asked to determine the analytes of interest by methods of their choice and expertise. Six replicate determinations were requested in the IAEA program, whereas five were requested by CCRMP.

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1. To be reported in entirety in a future CANMET CCRMP Report.
2. Prepared by CCRMP for IAEA in November, 1986.

Following completion of the IAEA program, the results sets were sent to CANMET for determination of recommended values of thorium, uranium, equivalent uranium and potassium in combination with the values obtained for these elements through the CCRMP program.

The contributing laboratories and corresponding personnel are listed alphabetically in the Appendix. The laboratory reference numbers are coded in the tables of this report in a manner which is uncorrelated with the alphabetic sequence.

RESULTS

The results for thorium, uranium, radium-226 (expressed as equivalent uranium) and potassium are compiled in Tables 5 to 8 together with laboratory set means and calculated standard deviations (S.D.) of the individuals from the mean values. The methodology used by each laboratory is indicated by a three letter acronym ("GAM" for gamma-ray spectrometry, "ICP" for inductively-coupled emission spectrometry, etc.) which is defined in Tables 9 to 12, where the available information as to methodology is summarized.

Analytical results for thorium, %, from the IAEA program were converted to equivalent thorium oxide, %, (by multiplication by 1.1379) to conform with the CCRMP reporting format.

Similarly, analytical results reported as uranium/radium mass ratios were converted to radium values in equivalent uranium units eU ug/g (assuming uranium-238/radium-226 secular equilibrium conditions), to yield a unit more amenable to comparison to the direct uranium measurements. The constant (k) 2.962×10^6 ug eU per ug radium-226[1], the mean uranium concentration ($\bar{U}$), uranium/radium mass ratio values (R) reported by the laboratory were used for the conversion, radium (eU) = $k\bar{U}/R$.

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1. The value of this constant is based on specific activities of $3.657 \times 10^{*}$ Bq/ug and $1.24365 \times 10^{**2}$ Bq/ug for radium-226 and uranium-238, respectively, and a uranium-238 abundance of 0.99274.

METHOD OF ASSESSMENT OF RESULTS

Model of Assessment

For each element, a one way analysis of variance technique was used to estimate the consensus value and its variance. This approach considers the results of the described certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (4).

$$x_{ij} = \mu + y_i + e_{ij}$$

where x_{ij} = the j^{th} result in set i,

μ = the true consensus value,

y_i = the discrepancy between the mean of the results in set i ($\bar{x}_i.$) and μ, and

e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i.$

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variances of ω^2 and σ^2, respectively. The significance of ω^2 is detected by comparing the ratio of between-sets means squares to within-set mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

The consensus value of the assumed model is estimated by the overall mean $\bar{x}..$:

$$\bar{x}.. = \sum_{i}^{k} \sum_{j}^{n_i} x_{ij} \Big/ \sum_{i}^{k} n_i$$

where n_i = the number of results in set i, and k = the number of sets.

The value of σ^2 is estimated by s_1^2 which is given by

$$s_1^2 = \sum_{i}^{k} \sum_{j}^{n_i} (x_{ij} - \bar{x}_i.)^2 / (\sum_{i}^{k} n_i - k).$$

The value of ω^2 is estimated by:

$$\omega^2 = (s_2^2 - s_1^2)/\frac{1}{k-1}\left(\sum_i^k n_i - \sum_i^k n_i^2 / \sum_i^k n_i\right)$$

where

$$s_2^2 = \sum_i^k n_i (\bar{x}_i. - x..)^2 / (k-1).$$

The variance of the overall mean is given by:

$$V[\bar{x}..] = \left(\sum_i^k n_i^2/(\Sigma n_i)^2\right) \omega^2 + \left(\sum_i^k 1/\Sigma n_i\right)\sigma^2$$

and the 95% confidence limits for x.. are

$$\bar{x}.. \pm t_{0.975,(k-1)}\sqrt{V[\bar{x}..]}$$

It should be noted that the 95% confidence limits denote that if the certification program were performed 100 times, the overall mean would be expected to fall within the prescribed limits 95 times.

The average within-set standard deviation, σ_A, where

$$\sigma_A = \frac{1}{k}\sum_i^k \sqrt{\sum_j^{n_i} (x_{ij} - x_i.)^2/(n_i-1)},$$

is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists therefore that a laboratory using a method of average or better repeatability should obtain individual results for a given certified element with a precision that is at least comparable to the reported value of σ_A.

Detection of Outliers

Sets deemed to have a low probability of belonging to the universe of the consensus model were removed prior to the calculation of the consensus mean and its associated uncertainty. Such outlier sets were identified in two steps. First, sets having inordinately deviate means were removed without recourse to statistical tests. It is likely that there is an

identifiable physical or mathematical reason for the magnitude of the deviations in these cases, for example, a severe methodological interference or calculation error, but this may only be verified by the laboratories concerned.

Following the removal of grossly outlying sets, the mean and standard deviation (σ) of individuals from the mean were computed for all remaining data. Sets having means beyond 2σ from the overall mean were examined for Dixon outliers (5). These were removed, if detected, and the set mean was recalculated. If the set mean remained beyond 2σ from the overall mean, the set was declared a "2σ" outlier and removed from the subsequent calculations of the consensus mean and its associated statistical parameters.

Criteria for Certifiability

The CCRMP has adopted two criteria to assess if the degree of consensus between laboratories is sufficient to warrant certification of the consensus mean value (6,7). Formerly, the test applied for certifiability was that the ratio of the spread (95% confidence interval as a percentage of the consensus value) to the average within-set coefficient of variation be less than four and the number of accepted sets be ten or more. This certification factor (CF) was subsequently replaced by a new certification criteria. In this test, the sets having extreme mean values are removed sequentially until the ratio of the between-to average within-laboratory standard deviations falls below three. The test parameter is RP, the percentage of sets rejected, and the criterion for certifiability is RP < 15% and ten or more accepted sets. Sets identified as physical outliers are excluded in the application of this test.

DISCUSSION OF RESULTS

The results of statistical assessments for thorium oxide and uranium are presented in Tables 13 and 15. The data acquired in the IAEA and CCRMP measurement projects were assessed independently in order to ascertain the "between-projects" consensus. For both thorium and uranium the consensus means from the two projects agreed well within their respective 95%

confidence limit estimates. For purposes of determining the recommended values, all the data from the two projects were therefore combined. Since several laboratories contributed to both projects, one of each of these duplicate sets was removed for the combined assessments.

Results for Thorium

The consensus value, obtained as the mean of 155 accepted results from 29 laboratory sets is 3.292±0.066 % ThO_2, or 2.893±0.058 % Th, where the uncertainty is a 95% confidence interval estimate for the mean. Two of the thirty-one sets submitted were rejected as outliers in obtaining this result. The consensus values meet the criteria for certifiability by CCRMP as RP is less than 15% and more than ten sets were acceptable.

Means by method and associated statistical parameters for the accepted sets for thorium oxide are compared in Table 14. There is no substantial evidence for any relative methodological bias. It is of interest that the gamma-ray radiometric determinations are in excellent agreement with other methodologies in view of the intended usage of OKA-2 for gamma-ray radiometric calibration.

Results for Uranium

Measurements of equivalent uranium based on measurement of radium-226 (or its rapidly equilibrated daughters) require radiometric equilibrium in the uranium-238 series for these measurements to reflect the actual uranium concentration. These results were therefore assessed independently of direct uranium measurements initially. The sets of direct measurements from IAEA and CCRMP were also assessed separately to examine the degree of consensus between projects.

As may be seen from Table 15, the consensus values are substantially the same from the three assessments, that is, within the overlapping limits of their 95% confidence uncertainty estimates. One obtains 0.974±0.172 and 0.979±0.114 for the equivalent uranium (radium)/uranium ratio using the IAEA and CCRMP uranium data respectively. Consequently it is inferred that radium-226 is in equilibrium with uranium-238 and that the radiometric measurements are valid measurements of uranium.

The result of the combined data analysis yields a consensus value of 218.6±8.2 ug/g uranium in OKA-2. The consensus is the result of 145 results obtained from 27 accepted sets. Six of thirty-three sets submitted were rejected as outliers in this assessment. The consensus value and its uncertainty meets the criteria for certifiability by CCRMP since RP is less than 15%, and more than ten sets were accepted.

Thorium/Uranium Ratio and IAEA Requirements

From the consensus values and their respective uncertainties the thorium/uranium mass ratio for OKA-2 is 132.3±5.6 (95% confidence interval). This substantially exceeds the minimum requirement of 100 for this ratio set by the IAEA consultants committee for a suitable calibration material for radiometric measurements of thorium (3).

Results for Potassium

Of the ten results sets for potassium, two were declared to be gross outliers, perhaps due to decimal reporting errors. Unfortunately, this leaves less than the minimum number of sets considered necessary for certification by CCRMP, and the results must be considered provisional, pending more information. The statistical assessment is presented in Table 16, yielding 0.344±0.022 % potassium as the mean of 45 accepted results.

Application of OKA-2 in Assessment of Methodology for Thorium or Uranium

Tables 13 and 15, contain values for the statistical parameters S_{rc} and S_{Lc} and the respective degrees of freedom associated with the calculation of each parameter. S_{rc} and S_{Lc} are identical to σ and ω, respectively as described previously under "Model of Assessment", and represent standard deviations within-and between-laboratories, respectively. These parameters are proposed to be used to assess the quality of a method applied by a laboratory relative to those accepted in an interlaboratory measurement program in application to the reference material (8).

In these tests, the laboratory performs n replicate measurements (ten is recommended as minimal) and determines the mean value for the concentration ($\bar{x}$) and the within-laboratory standard deviation (S_w). The

ratio $(S_w/S_{rc})^2$ is then compared to the F statistic at 95% for (n-1) and DF (S_{rc}) degrees of freedom. If the ratio is below the critical value, the method is deemed to have acceptable precision. Secondly, the value $|\bar{X} - A_c|$ is computed, where A_c is the certified value for the reference material. If $|X - A_c|$ is less than 2 S_{Lc}, the method is regarded as having acceptable accuracy, in comparison with methods used to obtain the certified value.

CONCLUSION

OKA-2 is a reference material certified by CCRMP by interlaboratory consensus to have 2.893±0.058 % thorium and 218.6±8.2 µg/g uranium. The uncertainties represent 95% confidence interval estimates for the means of these values for repetitions of similar programs.

OKA-2 meets the criteria of IAEA as a source material suitable to prepare a gamma-ray spectrometry calibration standard for thorium having a certified thorium content, thorium-232 series radiometric equilibrium, a high thorium/uranium ratio (132.3±5.6) and a high thorium/radiometric potassium ratio.

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Members of the staff of the Radiation Geophysics section, Resource Geophysics and Geochemistry Division, Geological Survey of Canada located, acquired and initially characterized the source material for OKA-2 and subsequently made this material available to CCRMP.

P. Westra and D.G. McIntosh of the Reference Materials Section, Chemical Laboratory, Mineral Sciences Laboratories comminuted, blended and bottled OKA-2 and handled its distribution for CCRMP.

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APPENDIX

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Table 1 - Wet screen analysis of OKA-2

Mesh Sizes (Tyler)	Particle Size (μm)	Wt %
-100 to +200	150 to 75	0.1
-200 to +325	75 to 45	18.4
-325 to +400	45 to 38	11.7
-400	less than 38	69.8

Table 2 - Approximate chemical composition of OKA-2

Component	%
$RE_2O_3+Y_2O_3$	33.5[1.]
CaO	25.32
SiO_2	14.72
P_2O_5	8.93
Fe_2O_3	5.83
ThO_2	3.29[2.]
F	1.28
MgO	1.24
Al_2O_3	0.82
SrO	0.66
MnO	0.52
ZnO	0.55
NiO	0.16
TiO_2	0.62
Na_2O	0.36
C	0.32
U_3O_8	0.0258[2.]

1. Sum of values for rare earth oxides determined individually.
2. Certifiable values from interlaboratory measurement program.

Table 3 - Measurements of thorium by X-ray fluorescence spectrometry to confirm homogeneity of OKA-2*

Bottle No.	Counts/second, thorium Lα		
	Subsample A	Subsample B	Subsample C
39	4641	4612	4673
91	4652	4657	4604
143	4640	4632	4602
195	4591	4613	4632
247	4638	4694	4628
299	4673	4629	4623
351	4678	4694	4621
304	4632	4684	4608
455	4667	4651	4637
507	4630	4656	4635
559	4650	4614	4672
611	4642	4614	4633
663	4635	4667	4669
715	4624	4611	4685
769	4630	4672	4659
Overall mean: 4637.867			

* Thorium Lα fluorescence measured for 20s. Philips PW1400 Spectrometer with Mo tube excitation and Li220 analysing crystal (2Ø = 39.23°).

Table 4 - Analysis of variance of thorium measurements

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F-ratio
Between-bottles	14	8.0459E03	5.747E02	0.670*
Within-bottles	30	2.5733E04	8.578E02	
Total	44	3.3779E04		

* Since the calculated F-ratio is less than the tabulated critical value Fα = 0.05 of 2.037, the null hypothesis of no difference between bottles is accepted.

Table 5 Analytical results, set means and standard deviations for thorium in OKA-2 (as thorium oxide).

Labor.	Method	Subsample Result, ThO2 %						Mean	S.D.
IAEA-1	GAM	3.228	3.246	3.200	3.226	3.199	3.177	3.213	0.025
IAEA-2	ICP	3.243	3.209	3.277	3.163	3.163	3.186	3.207	0.046
IAEA-3	COL	3.266	3.254	3.277	3.277	3.391	3.163	3.271	0.073
IAEA-4	GAM	3.152	3.163	3.163	3.152	3.175	3.175	3.163	0.010
IAEA-4	XRF	3.015	3.015	2.970	3.061	3.175	3.061	3.050	0.070
IAEA-5	NAA	3.175	3.266	3.118				3.186	0.075
IAEA-6	TIT	3.260	3.308	3.281	3.304	3.304	3.272	3.288	0.020
IAEA-7	COL	3.375	3.450	3.400	3.500	3.375	3.425	3.421	0.049
IAEA-8	DNC	3.141	3.186	3.175	3.050	3.232	3.198	3.164	0.063
IAEA-9	GAM	3.288	3.277	3.289	3.300	3.289	3.288	3.289	0.007
IAEA-10	GAM	(individual values not reported; std. additions, 6 samples)						3.600	0.05
IAEA-11	NAA	3.391	3.084**	3.391	3.53	3.39	3.53	3.446	0.076
IAEA-12	XRF	3.502	3.493	3.512	3.494	3.507	3.496	3.501	0.008
IAEA-13	NAA	2.879	2.981	2.913	2.879	2.879	2.981	2.919	0.050
IAEA-14	NAA	3.721**	3.482	3.414	3.516	3.516	3.459	3.477	0.043
IAEA-15	GAM	3.391	3.488	3.436	3.380	3.345	3.323	3.394	0.060
CCRMP-1	XRF	3.30	3.299	3.297	3.30	3.30		3.299	0.001
CCRMP-2	COL	2.98	3.01	3.21	3.11	3.22		3.106	0.111
CCRMP-3	GAM	(individual values not reported; std. additions, 6 samples)						3.600	0.05
CCRMP-4	XRF	3.345	3.357	3.368	3.391	3.345		3.361	0.019
CCRMP-5	NAA	3.39	3.39	3.5	3.39	3.5		3.434	0.060
CCRMP-6	NAA	3.38	3.38	3.37	3.44	3.36		3.386	0.031
CCRMP-7	XRF	3.463	3.440	3.517	3.512	3.483		3.483	0.033
CCRMP-8	NAA	3.528	3.562	3.630	3.493	3.641		3.571	0.064
CCRMP-9	ICP	3.4	3.4	3.4	3.4	3.3		3.38	0.045
*CCRMP-10	NAA	2.708	2.739	2.594	2.707	2.640		2.678	0.059
CCRMP-11	GAM	3.37	3.34	3.36	3.37	3.44		3.373	0.038
CCRMP-12	NAA	3.17	3.27	3.12	3.19	2.94		3.138	0.123
CCRMP-13	NAA	3.050	2.993	2.879	2.959	2.708		2.918	0.133
CCRMP-14	NAA	3.38	3.43	3.39	3.40	3.52		3.424	0.057
*CCRMP-15	NAA	2.72	2.663	2.708	2.742	2.708		2.708	0.029
CCRMP-16	ICP	3.664	3.209	3.391	3.368	3.562		3.439	0.178
CCRMP-17	XRF	3.198	3.198	3.175	3.198	3.220	3.220	3.206	0.019
		3.232							
CCRMP-18	DCP	3.259	3.314	3.370	3.326	3.336		3.321	0.040
CCRMP-19	GAM	3.228	3.246	3.200	3.226	3.199	3.177	3.213	0.025

* Declared outlier sets.
** Dixon outlier values (within-set).

Table 6 Analytical results, set means and standard deviations for uranium in OKA-2.

Labor.	Method	Subsample Result, U ug/g						Mean	S.D
IAEA-2	FLU	220.	230.	240.	240.	225.	230.	230.8	8.0
IAEA-3	COL	203.	212.	212.	210.	211.	210.	209.7	3.4
IAEA-4	COL	207.	219.	207.	219.	205.		211.4	6.9
IAEA-5	DNC	232.	236.	240.				236.0	4.0
IAEA-6	COL	217.	218.	227.	220.	224.	225.	221.8	4.1
*IAEA-7	FLU	329.	313.	308.	306.	301.	319.	312.9	10.0
*IAEA-8	DNC	154.	138.	140.	144.	139.	139.	142.3	6.1
IAEA-8	GAM	220.	198.	222.	198.	211.	222.	211.8	11.5
IAEA-11	DNC	230.	227.	217.	221.	222.	229.	224.3	5.1
IAEA-12	COL	267.	267.	264.	266.	269.	267.	266.7	1.6
IAEA-13	DNC	217.	230.	214.	212.	211.	224.	218.0	7.5
*IAEA-14	DNC	129.	127.	120.	149.	133.	143.	133.5	10.7
CCRMP-2	FLU	220.	210.	220.	200.	220.		214.0	8.9
CCRMP-4	FLU	201.	216.	196.	224.	198.		207.0	12.3
CCRMP-5	DNC	230.	227.	221.	222.	229.		225.8	4.1
CCRMP-6	DNC	250.	259.	257.	263.	261.		258.0	5.0
CCRMP-7	XRF	220.	210.	170.	220.	260.		216.0	32.
CCRMP-8	NAA	196.	214.	206.	156.	232.		200.8	28.
CCRMP-10	NAA	189.	226.	171.	177.	203.		193.2	22.
CCRMP-12	NAA	236.	230.	232.	242.	234.		234.8	4.6
CCRMP-13	NAA	227.	234.	236.	238.	214.		229.8	9.8
CCRMP-14	NAA	221.	227.	212.	223.	230.		222.6	6.9
CCRMP-15	NAA	233.1	237.8	228.3	234.3	223.4		231.4	5.6
CCRMP-16	FLU	185.	195.	185.	175.	175.		183.0	8.4
*CCRMP-18	FLU	700.	800.	700.	400.	400.		600.	187.

* Declared outlier sets.

Table 7 Analytical results, set means and standard deviations for radium in OKA-2 (as equivalent uranium).

Labor.	Method	Subsample Result, 226Ra (eU, ug/g)						Mean	S.D.
IAEA-3	GAM	223.	236.	241.	208.	218.	218.	224.0	12.3
IAEA-4	GAM	218.	215.	219.	217.	219.	217.	217.7	1.5
IAEA-5	GAM	232.	236.	238.				235.3	3.1
IAEA-6	SCI	211.4	205.7	207.4	210.6	207.4	209.0	208.6	2.2
IAEA-8	GAM	229.	255.	223.	253.	238.	224.	237.0	14.2
*IAEA-11	SCI	1250.	1300.	1440.	1190.			1295.	107.
*IAEA-14	GAM	3700.	3470.	3730.	2450.	3300.	2910.	3260.	498.
IAEA-15	GAM	186.	161.	190.	129.	167.	196.	171.5	24.9
CCRMP-11	GAM	196.	200.	200.	195.	202.		198.6	3.0

* Declared outlier sets.

Table 8 Analytical results, set means and standard deviations for potassium in OKA-2.

Labor.	Method	Subsample Result, K %						Mean	S.D.
IAEA-2	AAS	0.312	0.298	0.305	0.300	0.306	0.302	.304	.0050
IAEA-3	AAS	0.362	0.358	0.345	0.361	0.375	0.364	.361	.0097
IAEA-4	AAS	0.370	0.360	0.370	0.370	0.380	0.370	.370	.0063
*IAEA-5	AAS	0.030	0.033	0.029				.0307	.0021
IAEA-6	AAS	0.307	0.308	0.310	0.319	0.322	0.327	.316	.0083
IAEA-7	AAS	0.366	0.374	0.331	0.367	0.413	0.357	.368	.0268
IAEA-12	AAS	0.358	0.351	0.352	0.349	0.355	0.355	.353	.0033
*CCRMP-2	AAS	0.04	0.05	0.04	0.04	0.04		.042	.0045
CCRMP-7	AAS	0.33	0.33	0.33	0.34	0.33		.332	.0045
CCRMP-18	DCP	0.354	0.347	0.353	0.347			.350	.0039

* Declared outlier sets.

Table 9 - Summary of analytical methods for thorium

A. Gamma-ray spectrometry (GAM)

Laboratory	Subsample (g)	Detail
IAEA-1 (CCRMP-19)	7	5X5" NaI(Tl) spectrometry; ^{208}Tl at 2.62 meV measured; 1906-refined thorium nitrate calibrant. Ampoule-sealed samples.
IAEA-4	30	Ge(Li) spectrometry; 9 photopeaks of ^{228}Ac, ^{212}Pb, ^{212}Bi and ^{208}Tl measured. Al can-sealed samples.
IAEA-9	20	High-resolution spectrometry; ^{228}Ac, ^{224}Ra, ^{212}Bi and ^{208}Tl photopeaks measured; NBL reference materials employed for calibration.
IAEA-10 (CCRMP-3)	10	Ge(Li) spectrometry, ^{208}Tl at 911 KeV measured aliquots of ThO_2. Corrected for ^{228}Ac/^{232}Th ratio of ThO_2 as measured with alpha spectrometry.
IAEA-15	10	Ge(Li) spectrometry; 5 photopeaks of ^{228}Ac and ^{208}Tl measured; calibration by aliquot additions of thorium nitrate with correction for ^{228}Ac/^{232}Th ratio of spike obtained by comparison to 1906-refined material. Steel can-sealed samples.

B. Plasma emission spectrometry (ICP or DCP)

Laboratory	Subsample (g)	Detail
IAEA-2	0.125	Sample fused with 1g $LiBO_2$; pellet dissolved in 6% HNO_3 and diluted to 50 mL. An aliquot was diluted 10 fold for ICP measurements at 401.91 nm.
CCRMP-9	1.00	Sample fused with 1.5g of $LiBO_2/Li_2B_4O_7$ (2:1); melt dissolved in dilute HNO_3 (1:1) with 0.4% EDTA; filtered and diluted to 250 mL. Aliquots measured by ICP at 283.73 nm. Matrix-matched standards used for calibration.
CCRMP-1	3.00	
CCRMP-16	0.250	Acid digestion (HNO_3/HF/$HClO_4$); evaporation; dilution to 25 mL with 0.5M HCl for ICP measurement.
CCRMP-18	0.200	Acid digestion (HNO_3/HF/$HClO_4$); evaporation dilution in HCl medium for ICP measurements

Table 9 - (cont'd)

C. Spectrophotometric methods (COL)

Laboratory	Subsample (g)	Detail
IAEA-3	0.200	Acid digestion (HF/H_2SO_4). Separation of thorium by anion exchange from 10M HCl; dilution of eluant to 250 mL. Aliquots of 250 µL treated to form arsenazo (III) complex, measured at 665 nm.
IAEA-7	0.200	Sample fused with 5g $Na_2B_4O_7$; melt dissolved in 10% HCl and diluted volumetrically. Determined as thoron complex using method of additions for calibration.
CCRMP-2	1.00	Decomposition and spectrophotometric determination as thoron complex: [J.A. Maxwell, "Rock and Mineral Analysis"(1980)].

D. X-ray fluorescence spectrometry methods (XRF)

Laboratory	Subsample (g)	Detail
IAEA-4	0.400	Wavelength-dispersive XRF measurements of pressed powder pellets.
IAEA-12	0.250	Fused with flux to form glass beads for measurement; calibration by method of additions.
CCRMP-1	3.00	Energy-dispersive XRF of Th K with ^{57}Co excitation and a Ge(Li) detector. Pressed powder pellets with reference ore calibration; applied matrix absorption and spectral interference corrections.
CCRMP-4	4.00	XRF measurements of pressed powder pellets with reference ore calibration.
CCRMP-7	0.13	XRF measurements of pressed powder pellets with internal standardization.
CCRMP-17	1.00	Acid digestion of samples followed by precipitation of hydrous oxides and fluorides successively. Fluorides were fused with $Li_2B_4O_7$ and Th determined by wavelength dispersive XRF.

Table 9 - (cont'd)

E. Neutron activation analysis (NAA) and delayed neutron counting (DNC)

Laboratory	Subsample (g)	Detail
IAEA-5	0.500	See CCRMP-12
IAEA-8	0.600	DNC with two irradiations with and without Cd shield to obtain both U and Th. Thorium nitrate on solid substrate for calibration.
IAEA-11	2.00	^{223}Pa at 311 KeV measured following irradiation in thermal neutron flux, and a decay period.
IAEA-13	0.020	^{232}Pa at 311 KeV measured following irradiation in a thermal neutron flux and an 8 day decay period.
IAEA-14	0.200	^{233}Pa measured following irradiation.
CCRMP-5		Irradiation for 1m followed by 192 h decay prior to measurement of ^{233}Pa at 312 KeV.
CCRMP-6	0.500	Measurement of ^{233}Pa at 311 KeV after 7, 10 and 30 day decay periods. Both internal standards and reference sample calibration were applied to ascertain and correct for self-shielding.
CCRMP-8	0.01-0.02	Samples diluted with 0.5g SiO_2 prior to irradiation in a thermal neutron flux. Reference materials GSP-1, BCR-1, G-2 and AGV-1 used for calibrations.
CCRMP-10	0.100	Samples diluted with 60g lactose and five 0.5g samples irradiated. Calibration with reference material SRM 1632a and single element liquid standards.
CCRMP-12	0.200	No dilution; laboratory suspected self-shielding could cause their results to be low.
CCRMP-13	0.07-0.500	Samples were configured in a thin geometry (approx. 6cm^2 area) to reduce self-shielding).
CCRMP-14	0.100	Samples irradiated both in natural flux and with epi-calcium neutrons. Calibration with mono-element standards.

Table 9 - (cont'd)

F. Titrimetric method (TIT)

Laboratory	Subsample (g)	Detail
IAEA-6	0.100	Samples were fused with Na_2O_2 and the melt was dissolved in 1M HNO_3 containing 2% Al_2O_3. Thorium was separated from interferents by extraction chromatography or di-1-methylheptylmethyl phosphonate and determined by titration with EDTA at pH 1.5-2.0 with a xylenol orange indicator.

Table 10 - Summary of analytical methods for uranium

A. Fluorimetric methods

Laboratory	Subsample (g)	Detail
IAEA-2	0.500	Samples fused with $LiBO_2$ and melt dissolved in 6% HNO_3 followed by dilution to 50 mL. Aliquots of 100 µL were fused with NaF for fluorimetry.
IAEA-7	6.00	Acid digestion (HF/HNO_3); evaporation to dryness; and residue dissolved in HNO_3 and diluted to 50 mL. Aliquots treated for fluorimetry. Reference material DL-1a used for calibration.
CCRMP-2	1.00	Methodology as described in "Rock and Mineral Analysis" by J.A. Maxwell (1980).
CCRMP-4	1.00	Acid digestion (HF/HNO_3). Extraction of U into ethyl acetate from $Al(NO_3)_3$ containing aqueous phase. Aliquot of the extract fused with $Na_2CO_3/K_2CO_3/NaF$ flux for fluorimetry.
CCRMP-16	0.250	Acid digestion ($HF/HNO_3/HClO_4$); digest dissolved in 0.5M HCl. Aliquots taken for fluorimetry.
CCRMP-18	0.200	Acid digestion (HNO_3).

B. Spectrophotometric methods (COL)

Laboratory	Subsample (g)	Detail
IAEA-3	0.500	Acid digestion with $HNO_3/HCl/H_2SO_4$. Digest dissolved in 2M HNO_3, filtered and insol discarded. Solvent extraction into TBP/kerosene, extract washed with 5% KIO_3 in HNO_3, and U back-extracted into 25% $(NH_4)_2SO_4$. U extracted into 1% oxine and $CHCl_3$ and measured spectrophotometrically at 383 nm.
IAEA-4	0.500	Acid digestion with $HNO_3/HF/H_2SO_4$. Digest taken up in DTPA-containing medium and uranium was adsorbed on silica gel, and subsequently determined as the arsenazo-III complex.
IAEA-6	0.100	Fusion with Na_2O_2. Melt dissolved in HNO_3, Extraction chromatography on di-1-methylheptyl-methyl phosphonate to remove interferants. Uranium determined as 5-Br-PADAP complex at pH 4.8.
IAEA-12	2.00	Acid digestion with $HNO_3/HF/HClO_4$. Extraction into ethylacetate medium and determination of U as the dibenzoylmethane complex in pyridine medium.

Table 10 - (cont'd)

C. Neutron activation (NAA) and delayed neutron capture methods (DNC)

Laboratory	Subsample (g)	Detail
IAEA-5	0.050	DNC with correction for thorium interference.
IAEA-8	0.60	DNC, irradiation with and without Cd shielding to correct for thorium.
IAEA-11	0.500	DNC.
IAEA-13	0.020	DNC with 20s decay to eliminate ^{17}N interference. A correction of 30% was applied for ^{232}Th fission interference.
IAEA-14	0.200	DNC irradiation with and without Cd shielding to correct for thorium interference.
CCRMP-5		DNC.
CCRMP-6	0.500	DNC.
CCRMP-10	0.100	Sample blended with 60g lactose and 0.5g aliquots irradiated for NAA measurement. Reference material NBS SRM 1632a used for calibration, verified by single element solution standard. Confirmed by photon activation measurement (PHo) with comparison to SRM 1632a and SRM 1648.
CCRMP-12	0.200	NAA. Laboratory suspects results may be low due to sample self-adsorption.
CCRMP-13	0.070-0.0500	NAA. Samples irradiated in a thin geometry (6 cm^2) to minimize self-absorption effects.
CCRMP-14	0.100	Samples irradiated with and without Cd shielding. Calibration with mono-element standards.
CCRMP-15		NAA.

D. Gamma-ray spectrometry method

Laboratory	Subsample (g)	Detail
IAEA-9	20.0	Short-half life daughters of uranium-238 measured.

Table 11 - Summary of analytical methods for (equivalent uranium)

A. Gamma-ray spectrometry methods (GAM)

Laboratory	Subsample (g)	Detail
IAEA-3	20.0	Samples sealed one month prior to measurement of ^{214}Pb and ^{214}Bi emissions by high resolution Ge spectrometry. Reference material NBs SRM104a used for calibration.
IAEA-4	30.0	Samples sealed in Al cans prior to measurement of ^{214}Pb and ^{214}Bi emissions (5 photopeaks), by high-resolution Ge(Li) spectrometry.
IAEA-5	10.0	
IAEA-9	20.0	New Brunswick Laboratory uranium reference materials used for calibration, of measurements by high-resolution spectrometry.
IAEA-14	10.0	Measurement by sodium-iodide (Tl) scintillation spectrometry.
IAEA-15	10.0	Measurement of ^{214}Pb and ^{214}Bi emissions (5 photopeaks) by high resolution Ge(Li) pectrometry.
CCRMP-11	56.0	Samples sealed one month in thin steel cans. Measurement of ^{214}Pb and ^{214}Bi emissions (3 photopeaks) by high resolution Ge spectrometry. Reference material NBS 4959 radium solution was used for calibration by dispersion on silica and by additions to the sample matrix.

B. Scintillation methods (SCI)

Laboratory	Subsample (g)	Detail
IAEA-6	1.00	Samples fused in Na_2O_2 and melt dissolved in HCl. Radium coprecipitated with $BaSO_4$. Precipitate dissolved in alkaline EDTA. Radon-222 and decay products measured with a scintillation chamber.
IAEA-11	1.00	Acid digestion of samples with H_3PO_4/HNO_3. Radium coprecipitated with $BaSO_4$. Precipitate dissolved and radon-222 and decay product emissions counted in a scintillation cell.

Table 12 - Summary of analytical methods for potassium (AAS AND DCP)

Laboratory	Subsample (g)	Detail
IAEA-2	0.125	Samples fused with 1g $LiBO_2$. Melt dissolved in 6% HNO_3 and volumetrically diluted to 50 mL for flame AAS measurement.
IAEA-3	0.500	Acid digestion ($HF/HNO_3/HClO_4$). Evaporate dissolved in 1M HCl, insoluble material filtered off, and the filtrate diluted to 100 mL. An aliquot was diluted for measurement, using standard additions. (AAS)
IAEA-4	0.500	Acid digestion ($HF/HNO_3/H_2SO_4$). (AAS)
IAEA-5	0.500	Acid digestion followed by flame AAS.
IAEA-6	0.100	Acid digestion ($HF/HNO_3/H_2SO_4$). Evaporate dissolved in 2% HNO_3. AAS measurement at 766.5 nm with a sodium-containing buffer. Standards were prepared in a matrix similar to samples.
IAEA-7	6.00	Acid digestion (HF/HNO_3). Evaporate dissolved in HNO_3 and diluted to 50mL. (AAS).
IAEA-12	2.00	Acid digestion ($HF/HNO_3/HClO_4$). (AAS).
CCRMP-2	0.100	Methodology described in "Rock and Mineral Analysis", J.A. Maxwell (1980). (AAS).
CCRMP-7	0.130	Acid digestion ($HF/HClO_4$). (AAS).
CCRMP-18	0.200	Acid digestion ($HNO_3/HF/HClO_4$). Evaporate dissolved in HCl and diluted volumetrically. Calibration with single element solutions confirmed with CCRMP Reference materials SY-2 and SY-3. (DCP emission spectrometry).

Table 13 - Statistical assessments of thorium in OKA-2

	Data Group		
	IAEA	CCRMP	Combined
Number of accepted sets	15	17	29
Number of accepted observations	80	84	155
Grand mean, ThO_2%	3.298	3.319	3.292
Upper 95% confidence limit, ThO_2%	3.380	3.407	3.357
Lower 95% confidence limit, ThO_2%	3.216	3.232	3.226
Spread, %	4.96	5.26	3.96
Average within-set coef. variation, σ_A%	1.39	1.90	1.65
Certification factor (CF)	3.57	2.77	2.41
Certification Criterion (RP' %)[1].	18.8	10.5	12.9
Sets excluded as outliers [2].	IAEA-13 (2σ,)	CCRMP-10(2σ,) CCRMP-15)2σ,)	CCRMP-10(2σ,) CCRMP-15(2σ,)
Sets excluded as duplicates	NA	NA	IAEA-5 IAEA-10 IAEA-11 CCRMP-19
S_{rc} or σ (DF)[3].	0.0498(65)	0.0764(67)	0.0647(126)
S_{Lc} or ω (DF)[3].	0.1427(14)	0.1637(16)	0.1672(28)

1. RP is the percentage of successive extremal sets required to be rejected in order to reduce the ratio of between-to within-set standard deviations below 3.

2. Outliers designated (G) were declared as outliers (due to a probable bias in methodology) without recourse to statistical tests. Remaining sets having mean values more than two standard deviations (of individual values) from the mean of all results were also declared outliers (2σ,).

3. S_{rc} and S_{Lc} are respectively the estimates of within- and between-laboratories standard deviations and DF is the corresponding degrees of freedom associated with each estimate.

Table 14 - Comparison of results for thorium oxide by different methodologies

Method	No. Sets	No. Values	Mean	Spread, %	Average C.V., %
NAA	10	52	3.279	10.5	2.2
XRF	6	34	3.307	11.2	0.8
GAM	5	29	3.283	7.6	0.9
COL	3	17	3.276	23.5	2.4
ICP	3	16	3.333	18.4	2.6
DCP	1	5	3.321	-	1.2
TIT	1	6	3.288	-	0.6

Table 15 - Statistical assessments of uranium in OKA-2

	Data Group			
	IAEA	CCRMP	Equiv. U	Combined
Number of accepted sets	12	13	7	27
Number of accepted observations	68	65	38	145
Grand mean, U, µg/g	217.6	216.5	211.9	218.6
Upper 95% confidence limit, U, µg/g	249.0	228.8	233.6	226.7
Lower 95% confidence limit, U, µg/g	186.2	204.3	190.2	210.4
Spread, %	28.9	11.3	20.5	7.42
Average within-set coefficient of variation, σ %	3.26	5.54	4.36	4.56
Certification factor	8.85	2.04	4.70(n.a.)	1.63
Certification criterion (RP%)[1].	3.33	0.0	0.0(n.a.)	6.7
Sets excluded as outliers [2].	none	CCRMP-18(G)	IAEA-11(G) IAEA-14(G)	IAEA-11(G) IAEA-14(G) CCRMP-18(G) IAEA-7($2\sigma_1$) IAEA-14($2\sigma_1$) IAEA-8($2\sigma_1$)
Sets excluded as duplicates	n.a.	n.a.	n.a.	IAEA-5(DNC) CCRMP-10(P40)
S_{rc}, or σ (DF)[3].	7.35(56)	14.8(52)	12.6(31)	12.4 (118)
S_{Lc}, or ω (DF)[3].	48.8(11)	19.1(12)	22.4(6)	19.6(26)

1. RP is the percentage of successive extremal sets required to be rejected in order to reduce the ratio of between-to within-sets standard deviations below 3.

2. Outliers designated (G) were declared as outliers (due to a probable bias in methodology) without recourse to statistical tests. Remaining sets having mean values more than two standard deviations (of individual values) from the mean of all results were also declared outliers ($2\sigma_1$).

3. S_{rc} and S_{Lc} are respectively the estimates of within-and between-laboratories standard deviations and DF is the corresponding degrees of freedom associated with each estimate.

Table 16 - Statistical assessment of potassium in OKA-2

Number of accepted sets		8
Number of accepted observations		45
Grand mean, K%		0.344
Upper 95% confidence limit		0.366
Lower 95% confidence limit		0.323
Spread %		12.4
Average within-set coefficient of variation		2.42
Certification Factor*		5.1
Certification criterion (RP%)*		20.0
Sets excluded as outliers		IAEA-5(G) CCRMP-2(G)
S_{rc}, or σ (DF)	0.01151	(37)
S_{Lc}, or ω (DF)	0.02488	(7)

* Since number of accepted sets is less than ten, certification by CCRMP was not considered.